

A Specialist Periodical Report

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# Electrochemistry

Volume 7

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A Review of Recent Literature

Senior Reporter

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## *Preface*

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To get the priorities right, the Senior Reporter again must express his thanks to the contributors who have found the time, in a busy professional life, to produce the chapters for Volume 7.

It is often commented in reviews of this series that sometimes the contents may not be up-to-date or that the coverage goes back over many years. There is without doubt a basis for this criticism but it would also seem to be inevitable. In recent years interest in electrochemistry has both widened and deepened; new areas require reporting, older fields continue to provide new material of value, but large monographs have become a formidable expense, and, if it is desirable that this and similar volumes should be a possible personal rather than a purely library acquisition, cost is of importance.

It would therefore seem inescapable, within a comparatively small book, to avoid the faults, but one would hope that this will continue to be recompensed by articles of depth on a variety of interests, even if only a few are covered each year but covered in the informed manner which hopefully is the mark of this series.

H R THIRSK

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## Organic Electrochemistry – Synthetic Aspects

BY J. GRIMSHAW

This Report covers material published during 1975. Papers dealing with physical organic chemistry, such as reaction mechanisms, which have a bearing on electrochemical synthesis are included. Studies of radical-ions by e.p.r. have been excluded, as have papers on electrochemically initiated polymerization, electrocoating, and related technical fields.

Abbreviations used throughout this chapter are as follows: AN, acetonitrile; DME, 1,2-dimethoxyethane; DMF, dimethylformamide; DMSO, dimethyl sulphoxide; HMPT, hexamethylphosphoric triamide; THF, tetrahydrofuran.

## 1 General

The coverage of electro-organic synthesis in the Techniques of Chemistry series was completed in 1975.<sup>1</sup> Anodic oxidation was surveyed in another book<sup>2</sup> and chapters on electrochemistry have appeared in textbooks on the chemistry of quinones<sup>3</sup> and of hydrazo-, azo-, and azoxy-groups.<sup>4</sup> Other books have covered electrode kinetics,<sup>5</sup> experimental electrochemistry,<sup>6</sup> and electrochemical data for organic, organometallic, and biochemical substances.<sup>7</sup> Reviews have appeared on general synthetic reactions,<sup>8</sup> the synthesis of cyclic compounds,<sup>9</sup> electroreduction,<sup>10</sup> oxidation,<sup>11</sup> the synthesis and reactions of organometallic compounds,<sup>12</sup> and industrial electrosynthesis,<sup>13</sup> including indirect electrochemical processes<sup>14</sup> and reactor design.<sup>15</sup> The use

<sup>1</sup> 'Techniques of Electro-organic Synthesis', ed. N. L. Weinberg, Wiley, New York, 1974.

<sup>2</sup> S. D. Ross, M. Finkelstein, and E. Rudd, 'Anodic Oxidation', Academic Press, New York, 1975.

<sup>3</sup> J. Q. Chambers in 'Chemistry of Quinonoid Compounds', ed. S. Patai, Wiley, Chichester, 1974, Part 2, p. 737.

<sup>4</sup> F. G. Thomas and K. G. Botoin, 'Chemistry of Hydrazo, Azo and Azoxy Groups', ed. S. Patai, Wiley, Chichester, 1975, Part I, p. 443.

<sup>5</sup> J. Albery, 'Electrode Kinetics', Oxford University Press, Oxford, 1975.

<sup>6</sup> D. J. Sawyer and J. L. Roberts, 'Experimental Electrochemistry for Chemists', Wiley, New York, 1974; E. Gileadi, E. Kirowa-Eisner, and J. Penciner, 'Interfacial Electrochemistry – An Experimental Approach', Addison-Wesley, Reading, Mass., 1975.

<sup>7</sup> L. Meites, P. Zuman, W. J. Scott, B. H. Campbell, and A. M. Kardos, 'Electrochemical Data. Vol. 1. Organic, Organometallic and Biochemical Substances. Pt A', Wiley, New York, 1974.

<sup>8</sup> T. Shono, *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, 1974, **42**, 542.

<sup>9</sup> M. Lacan and I. Tabakovic, *Kem. Ind.*, 1975, **24**, 227.

<sup>10</sup> M. Tarle, *Kem. Ind.*, 1974, **23**, 647; M. R. Rifi, *Tech. Chem. (N.Y.)*, 1975, **5**, 83.

<sup>11</sup> O. A. Petrii, *Usp. Khim.*, 1975, **44**, 2067; L. A. Mirkind, *ibid.*, p. 2088.

<sup>12</sup> G. A. Tedoradze, *J. Organomet. Chem.*, 1975, **88**, 1; W. J. Settineri and L. D. McKeever, *Tech. Chem. (N.Y.)*, 1975, **5**, 397.

<sup>13</sup> M. Fleischmann and D. Pletcher, *Chem. Br.*, 1975, **11**, 50; K. C. Narasimham and M. S. V. Pathy, *Chem. Eng. World*, 1975, **10**, 87.

<sup>14</sup> R. Clarke, A. Kuhn, and E. Okoh, *Chem. Br.*, 1975, **11**, 59.

<sup>15</sup> M. Fleischmann and R. E. W. Jansson, *Chem. Eng. (London)*, 1975, **302**, 603.

of ion-exchange membranes in electrochemical cells has been reviewed.<sup>16</sup> Electrochemistry in thin layers of solution is discussed in a critical review<sup>17</sup> and the application of electrochemistry to physical organic problems is discussed.<sup>18</sup> IUPAC have published recommendations for sign conventions and the plotting of electrochemical data.<sup>19</sup>

A process for the purification of HMPT by fractional freezing, vacuum distillation, and drying over calcium oxide has been described,<sup>20</sup> and the electrochemical properties of several other solvents have been evaluated. Oxydipropionitrile shows a large potential range for reductions at a mercury cathode but no reactions were studied in this solvent,<sup>21</sup> and a possible limitation is that electrogenerated bases will cause elimination to give acrylonitrile. Ethylene carbonate is liquid at 40°C and shows a good range for oxidation and reduction:<sup>22</sup> nitromethane<sup>23</sup> and 1,2-dichloroethane<sup>24</sup> are both satisfactory solvents for oxidation processes. Triethyl-n-hexylammonium triethyl-n-hexylboride is a new ambient-temperature molten-salt solvent with a useful working range for reduction, but the solvent readily undergoes oxidation.<sup>25</sup> A mixture of aluminium chloride (2 moles) and ethylpyridinium bromide (1 mole) is molten at ambient temperatures and forms a strong Lewis acid solvent that is useful for oxidation processes.<sup>26</sup> Quinones solubilized in micelles formed in aqueous sodium dodecylsulphate show well-defined diffusion waves on polarography.<sup>27</sup>

Advances in electronic apparatus for electrochemistry have been reviewed<sup>28</sup> and new designs proposed for function generators<sup>29</sup> and integrators.<sup>30</sup> New designs<sup>31,32</sup> for laboratory electrolysis cells are available. One of these is formed in a rolled sandwich construction of the two electrodes and a separator cloth.<sup>32</sup> The reaction solution is pumped through a tube packed with the sandwich, so that the substrate is in contact with both the cathode and anode. If the latter situation can be tolerated, then this cell design gives high flow rates and current densities. Porous Teflon has been proposed as a diaphragm material.<sup>33</sup>

Tungsten bronzes have been studied as electrode materials for use in both aqueous and aprotic solvents.<sup>34</sup> They have a large reduction and oxidation range.

<sup>16</sup> G. Richter, *Chem.-Ing.-Tech.*, 1975, **47**, 909.

<sup>17</sup> A. T. Hubbard, *Crit. Rev. Anal. Chem.*, 1973, **3**, 201.

<sup>18</sup> R. Breslow, *Pure Appl. Chem.*, 1974, **40**, 493.

<sup>19</sup> *Information Bull. IUPAC. Appendix: Provisional Nomenclature: Symbols, Units, Standardisation*, 1975, p. 42.

<sup>20</sup> M. G. Formicheva, Yu. M. Kessler, E. E. Zabusova, and N. M. Alpatova, *Elektrokhimiya*, 1975, **11**, 163.

<sup>21</sup> J. Y. Gal and M. Persin, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1975, **280**, 1305.

<sup>22</sup> J. Y. Cabon, M. L'Her, and M. LeDemezet, *Bull. Soc. Chim. Fr.*, 1975, 1020.

<sup>23</sup> M. Breant and G. Demange-Guerin, *Bull. Soc. Chim. Fr.*, 1975, 163.

<sup>24</sup> V. G. Mairanovskii, N. T. Ioffe, and A. A. Engovatov, *Elektrokhimiya*, 1975, **11**, 1303.

<sup>25</sup> W. T. Ford, *Anal. Chem.*, 1975, **47**, 1125.

<sup>26</sup> H. L. Chum, V. R. Koch, L. L. Miller, and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1975, **97**, 3264.

<sup>27</sup> T. Erabi, H. Hiura, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1354.

<sup>28</sup> P. Gilgen, K. Kaempf, and R. Rach, *Chimia*, 1975, **29**, 232.

<sup>29</sup> F. Magno, G. Bontempelli, G. A. Mazzocchin, and I. Patane, *Chem. Instrum.*, 1975, **6**, 239; D. F. Unterker, W. G. Sherwood, G. A. Martinchek, T. M. Reidhammer, and S. Bruckenstein, *ibid.*, p. 259.

<sup>30</sup> M. Lindstrom and G. Sundholm, *Finn. Chem. Lett.*, 1975, 27.

<sup>31</sup> P. Jeroschewski, *Ger. (East)* P. 111 158 (*Chem. Abs.*, 1975, **83**, 185 519).

<sup>32</sup> P. M. Robertson, F. Schwager, and N. Ibl, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **68**, 883.

<sup>33</sup> D. S. Riley and C. R. Vallance, *Ger. P.* 2 433 941 (*Chem. Abs.*, 1975, **83**, 68 083).

<sup>34</sup> M. Amjad and D. Pletcher, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **59**, 61.

Attempts have been made to improve the qualities of graphite as cathode material by coating it with mercury<sup>35</sup> and by attaching, with chemical bonds, a surface layer of (S)-(–)-phenylalanine methyl ester, bonded through the amine nitrogen.<sup>36</sup> The latter forms a chiral electrode surface which promotes the reduction of ketones to carbinols with partial asymmetric induction. Acetophenone afforded 1-phenylethanol for which  $[\alpha]_D$  ( $c=3$ ,  $\text{CHCl}_3$ ) was  $-7.2^\circ$ . However, other workers<sup>37</sup> were unable to repeat this claim of asymmetric reduction. The properties of platinized silica particles as a fluidized-bed electrode for the Kolbe reaction have been examined.<sup>38</sup>

Experimental and theoretical studies have been made on the effect of adsorption of neutral molecules on electrochemical reactions.<sup>39</sup> Cryptate complexes of alkali-metal ions are reduced at very negative potentials, but the potassium ion complex of kryptofix-[2,2,2] is strongly adsorbed at a mercury cathode from dilute solutions, which limits the use of this ion in conducting salts.<sup>40</sup>

General studies on the properties of redox reactions have included a study of the reversible oxidation and reduction of four polynuclear hydrocarbons at pressures up to 2000 atm.<sup>41</sup> The change in partial molar volume which accompanies the redox reaction can then be determined, and this gives information on the solvation changes which accompany electron transfer. When redox potential is determined by cyclic voltammetry, it is usually assumed that the ratio of diffusion coefficients for the redox species is sufficiently close to unity that its logarithm can be taken as zero. In a critical study of some aromatic radical-cations, the diffusion coefficient for the parent molecule was always found to be greater than for the cation, but the ratio could be taken as unity with sufficient accuracy.<sup>42</sup> A linear relationship has been shown between values of the electron affinity and the polarographic half-wave potentials for some cyclic anhydrides.<sup>43</sup> Polarography has been used to detect short-lived radicals and radical-cations that are generated by pulse radiolysis from anthracene, naphthalene, benzene, and acetone.<sup>44</sup>

Further papers have appeared on the use of convolution potential sweep voltammetry in the determination of electrochemical reaction mechanisms, including the acetophenone pinacolization, the intramolecular cyclization of 1,3-dibenzoylpropane, and the coupling of 4-methylbenzylidenemalononitrile.<sup>45</sup> The technique can also be used to determine standard electrode potentials where one part of the couple is unstable.<sup>46</sup>

<sup>35</sup> H. G. Tennant, U.S. P. 3 914 500 (*Chem. Abs.*, 1976, **84**, 23 763).

<sup>36</sup> B. F. Watkins, J. R. Belling, E. Kariv, and L. L. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 3549.

<sup>37</sup> L. Horner and W. Brich, *Justus Liebigs Ann. Chem.*, 1977, 1354.

<sup>38</sup> S. Yoshizawa, Z. Takehara, Z. Ogumi, and M. Matsubara, *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, 1975, **43**, 526 (*Chem. Abs.*, 1976, **84**, 81 627).

<sup>39</sup> J. Lipkowski and Z. Galus, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **61**, 11; H. Fischer, *ibid.*, 1975, **62**, 163.

<sup>40</sup> D. Britz and D. Knittel, *Electrochim. Acta*, 1975, **20**, 891; F. Peter and M. Gross, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **61**, 245.

<sup>41</sup> M. Fleischmann, W. B. Gara, and G. J. Hills, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **60**, 313.

<sup>42</sup> U. Svanholm and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 1975, 755.

<sup>43</sup> O. B. Nagy, H. Lion, and J. B. Nagy, *Bull. Soc. Chim. Belg.*, 1975, **84**, 1053.

<sup>44</sup> K. D. Asmus and M. Graetzel, *Nucl. Sci. Abs.*, 1975, **31**, 110.

<sup>45</sup> J. M. Savéant and D. Tessier, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **61**, 251; C. P. Andrieux, J. M. Savéant, and D. Tessier, *ibid.*, 1975, **63**, 429; L. Nadjo, J. M. Savéant, and D. Tessier, *ibid.*, 1975, **64**, 143.

<sup>46</sup> J. M. Savéant and D. Tessier, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **65**, 57.

Ultraviolet spectroscopy<sup>47</sup> has been used to study the intermediates in electrochemical reactions, and there is a developing interest in the application of resonance Raman spectroscopy to the detection of intermediates.<sup>48,49</sup> Thin carbon films deposited on germanium prisms form optically transparent electrodes suitable for i.r. spectroelectrochemistry.<sup>50</sup>

The contrasting colours of radical-ions and their neutral substrates have been made the basis of electrochromic display systems.<sup>51</sup> Electrochemiluminescence continues to be examined.<sup>52</sup>

## 2 Reduction

**General.**—Reduction of acetophenone in a chiral solvent, (*S*)-(+)-Me<sub>2</sub>NCH<sub>2</sub>CH(OMe)CH(OMe)CH<sub>2</sub>NMe, gives the same ratio of *meso* to ( $\pm$ )-pinacols and the same degree of asymmetric induction in the ( $\pm$ )-pinacol as is obtained by photo-reduction of acetophenone in the same solvent. This strongly suggests that dimerization occurs by the same step in the two reactions; i.e., by combination of two radicals Ph $\dot{\text{C}}\text{H}(\text{OH})\text{CH}_3$ .<sup>53</sup> Cobalt(III) trisacetylacetonate is destroyed on cathodic reduction, and the reaction in the presence of trimethyl-( $-$ )-menthylammonium perchlorate as supporting electrolyte was found to exhibit enantioselectivity.<sup>54</sup> The magnitude of this enantioselectivity varies systematically with potential and with electrolyte concentration.

A series of papers on mechanistic electrochemistry in liquid ammonia has appeared.<sup>55-57</sup> Liquid ammonia has a low dielectric constant, very low acidity, and is a suitable medium for reduction. In the absence of added protonating agents, nitrobenzene and nitrosobenzene are reduced by two reversible one-electron steps to the radical-anion and the dianion. In the presence of isopropyl alcohol as a weak acid, the dianion of nitrobenzene adds one proton and rapidly decomposes to nitrosobenzene. The dianion of nitrosobenzene adds one proton to give an anionic species which can be reversibly oxidized to the parent nitrosobenzene. In the presence of strong acids such as ammonium ions, both compounds are reduced to phenylhydroxylamine.<sup>55</sup> Quinoline is reduced in two one-electron steps, and the radical-anion dimerizes to a dianion, which can be re-oxidized to the parent quinoline.<sup>56</sup> Diethyl fumarate, cinnamionitrile, and acrylonitrile show similar electrochemical behaviour in liquid ammonia to that in aprotic solvents. Dimerization

<sup>47</sup> W. Paatsch, *Metalloberflaeche - Angew. Elektrochem.*, 1974, **28**, 485; A. Bewick, G. J. Edwards, and J. M. Mellor, *Tetrahedron Lett.*, 1975, 4685; W. J. Plieth and K. Naegele, *Electrochim. Acta*, 1975, **20**, 421.

<sup>48</sup> M. R. Suchanski and R. P. Van Duyne, *J. Am. Chem. Soc.*, 1975, **97**, 1699; D. L. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **66**, 235.

<sup>49</sup> A. J. McQuillan, P. J. Hendra, and M. Fleischmann, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **65**, 933.

<sup>50</sup> J. S. Mattson and C. A. Smith, *Anal. Chem.*, 1975, **47**, 1122.

<sup>51</sup> T. Kawata, M. Yamamoto, M. Yamana, M. Tajima, and T. Nakano, *Jpn. J. Appl. Phys.*, 1975, **14**, 725; I. F. Chang, B. L. Gilbert, and T. I. Sun, *J. Electrochem. Soc.*, 1975, **122**, 955; N. V. Philips, *Fr. P.* 2 228 262 (*Chem. Abs.*, 1975, **83**, 106 250).

<sup>52</sup> K. G. Boto and A. J. Bard, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **65**, 945; N. Periasamy and K. S. V. Santhanam, *Proc. Indian Acad. Sci., Sect. A*, 1974, **80**, 194.

<sup>53</sup> D. Seabach and H. A. Oei, *Angew. Chem.*, 1975, **87**, 629. (*Angew. Chem. Int. Ed. Engl.*, 1975, **14**, 634).

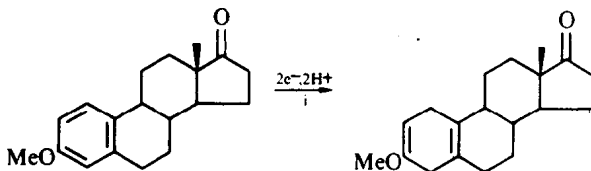
<sup>54</sup> S. Mazur and K. Ohkubo, *J. Am. Chem. Soc.*, 1975, **97**, 2911.

<sup>55</sup> W. H. Smith and A. J. Bard, *J. Am. Chem. Soc.*, 1975, **97**, 5203.

<sup>56</sup> W. H. Smith and A. J. Bard, *J. Am. Chem. Soc.*, 1975, **97**, 6491.

occurs by combination of radical-anions, and the rate is increased by the presence of potassium ions.<sup>57</sup>

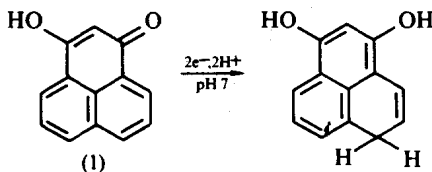
**Hydrocarbons.**—A patent has been issued for the reduction of aromatic steroids in a mixture of liquid ammonia and THF at a steel cathode (Scheme 1).<sup>58</sup> Trioxan has



Reagents: i, liquid  $\text{NH}_3$ , THF

Scheme 1

been suggested as a very useful solvent for the related reduction of benzene to cyclohexadiene at a mercury cathode.<sup>59</sup> The reduction of naphthalene in AN to 1,4-dihydronaphthalene has been patented.<sup>60</sup> 3-Hydroxyphenalenone (1) behaves in a manner like that of naphthalene on reduction in an aqueous buffer at a mercury cathode (Scheme 2), to give a dihydro-derivative.<sup>61</sup> Related to the reduction of



Scheme 2

benzenoid compounds is the electrosynthesis of 2,5-dihydrothiophen-2-carboxylic acid by the reduction, over a mercury cathode, of the lithium salt of thiophen-2-carboxylic acid.<sup>62</sup>

A full paper<sup>63</sup> has appeared describing the advantages of drying solvents over alumina actually in the electrolysis vessel, so as to stabilize the dianions from aromatic hydrocarbons. Under these conditions anthracene, benzanthracene, chrysenes, coronene, and perylene show reversible behaviour on cyclic voltammetry due to the formation of radical-anions and dianions. Cyclo-octatetraene shows two reversible one-electron reduction steps under these conditions, and the rate of charge transfer for addition of the first electron depends on the supporting tetraalkylammonium cation, being  $10^3$  times faster for  $\text{Me}_4\text{N}^+$  than for  $\text{Bu}_4\text{N}^+$ .<sup>64</sup> The

<sup>57</sup> I. Vartires, W. H. Smith, and A. J. Bard, *J. Electrochem. Soc.*, 1975, **122**, 894.

<sup>58</sup> K. Junghans, Ger. P. 2 337 155 (*Chem. Abs.*, 1975, **83**, 10 598).

<sup>59</sup> T. Hatayama, Y. Hamano, and K. Udo, *Jpn. P.* 74 41 192 (*Chem. Abs.*, 1975, **82**, 147 142).

<sup>60</sup> A. Misono, T. Cho, and H. Yamagishi, *Jpn. P.* 75 02 508 (*Chem. Abs.*, 1975, **82**, 161 873).

<sup>61</sup> J. C. Dufresne, *C.R. Hebd. Seances Acad. Sci., Ser. C.*, 1975, **280**, 1493.

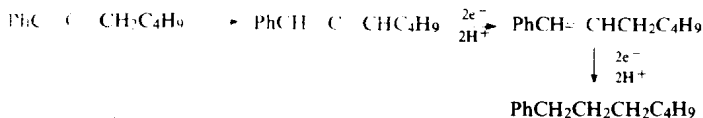
<sup>62</sup> V. S. Mikhailov, V. P. Gul'tyai, S. G. Mairanovskii, S. Z. Taitis, I. V. Proskurovskaya, and Yu. G. Dubovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 888 (*Chem. Abs.*, 1975, **83**, 87 240).

<sup>63</sup> B. S. Jensen and V. D. Parker, *J. Am. Chem. Soc.*, 1975, **97**, 5211.

<sup>64</sup> S. Jensen, A. Ronlan, and V. D. Parker, *Acta Chem. Scand., Ser. B*, 1975, **29**, 394; A. J. Fry, C. S. Hutchins, and L. L. Chung, *J. Am. Chem. Soc.*, 1975, **97**, 591.

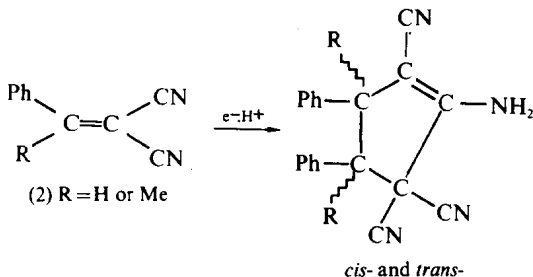
activation barrier for addition of the first electron, due to a conformational effect, is not as important as previously considered; electrolyte double-layer effects are greater than any conformational effects.

Polarography of 1-phenylhex-1-yne in DMF shows a single four-electron wave during which hexylbenzene is formed. However, under the conditions of preparative electrolysis, the isomerization of acetylene to allene becomes important, and the dominant process is reduction of the allene (Scheme 3).<sup>65</sup>



Scheme 3

**Activated Olefins.**—A number of patents<sup>66-68</sup> have appeared on the conversion of acrylonitrile into adiponitrile. A mechanistic study of the hydrodimerization of ethyl cinnamate and diethyl fumarate in DMF at room temperature and lower shows that the reaction proceeds in both cases *via* a radical-anion dimerization step.<sup>69</sup> Alkali-metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) greatly increase the rate of dimerization of dialkyl fumarates, ethyl cinnamate, and cinnamionitrile in DMF due to ion pairing with the radical-anions and then rapid dimerization of the ion pairs.<sup>70</sup> The unsaturated nitriles (2;  $\text{R} = \text{H}$ ) and (2;  $\text{R} = \text{Me}$ ) undergo irreversible one-electron reduction, with dimerization and then cyclization, in DMF, with or without an added proton source (Scheme 4); reaction between two radical-anions is proposed as the dimerization step.<sup>71, 72</sup> The related nitriles (2;  $\text{R} = \text{Bu}^t$ ) and (2;  $\text{R} = \text{Ph}$ ) show reversible radical-anion formation in DMF and further reduction to the dianion (Scheme 5). On addition of a proton donor, two-electron reduction to the dihydro-compound occurs at the potential of the first wave, and an *ECE* mechanism has been pro-



Scheme 4

<sup>65</sup> M. W. Moore and D. G. Peters, *J. Am. Chem. Soc.*, 1975, **97**, 139.

<sup>66</sup> M. Seko, A. Tokuyama, T. Isotani, K. Inada, and N. Matsumoto, *Jpn. P.* 75 02 492 (*Chem. Abs.*, 1975, **82**, 161 872).

<sup>67</sup> J. F. Connolly, U. S. P. 3 871 976 (*Chem. Abs.*, 1975, **83**, 68 077).

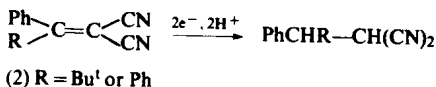
<sup>68</sup> M. Seko, Y. Takahashi, S. Ogawa, H. Iwashita, A. Yamaguchi, and H. Ide, *Jpn. P.* 75 05 171 (*Chem. Abs.*, 1975, **83**, 50 050); M. Seko, S. Ogawa, M. Yoshida, N. Oishi, S. Hazama, and K. Okubo, *Jpn. P.* 75 05 172 (*Chem. Abs.*, 1975, **83**, 50 051).

<sup>69</sup> R. D. Grypa and J. T. Maloy, *J. Electrochem. Soc.*, 1975, **122**, 377, 509.

<sup>70</sup> M. J. Hazelrigg and A. J. Bard, *J. Electrochem. Soc.*, 1975, **122**, 211.

<sup>71</sup> L. A. Avaca and J. H. P. Utley, *J. Chem. Soc., Perkin Trans. 2*, 1975, 161.

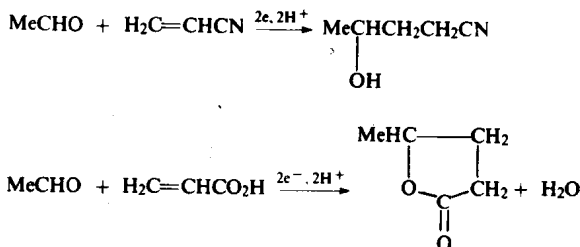
<sup>72</sup> L. A. Avaca and J. H. P. Utley, *J. Chem. Soc., Perkin Trans. 1*, 1975, 971.



Scheme 5

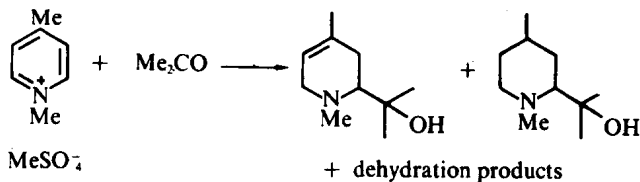
posed.<sup>71</sup> Electroreduction of  $\alpha\beta$ -unsaturated nitriles in acidic aqueous solution leads to the production of amines.<sup>73</sup>

Co-electrodimerization of carbonyl compounds with acrylonitrile in aqueous buffers leads to  $\gamma$ -hydroxy-nitriles,<sup>74, 75</sup> while a similar reaction with acrylic acid leads to  $\gamma$ -lactones (Scheme 6).<sup>76</sup>



Scheme 6

**Carbonyl Compounds.**—The mixed electrolytic reduction of 1,4-dimethylpyridinium methylsulphate and acetone leads to mixed coupling products (Scheme 7)



Scheme 7

along with products from reduction of the pyridine compound.<sup>77</sup> Patents<sup>78, 79</sup> have been issued for the electrolytic preparation of pinacols from simple aliphatic ketones, and in one process the corresponding secondary alcohol is used as the solvent.<sup>79</sup>

Two strikingly similar stereo- and enantio-selective hydrodimerization reactions have been described. Reduction of benzoin gives the racemic pinacol formed by *threo*-coupling between two molecules of the same enantiomeric configuration (Scheme 8).<sup>80</sup> Hydrodimerization of the racemic tricyclic enone (3) also gives the

<sup>73</sup> Yu. D. Smirnov, A. P. Tomilov, and S. K. Smirnov, *Zh. Org. Khim.*, 1975, 11, 522.

<sup>74</sup> A. P. Tomilov, B. L. Klyuer, and V. D. Nechepurnoi, *Zh. Org. Khim.*, 1975, 11, 1344.

<sup>75</sup> S. M. Makarochkina and A. P. Tomilov, *Zh. Obshch. Khim.*, 1974, 44, 2566.

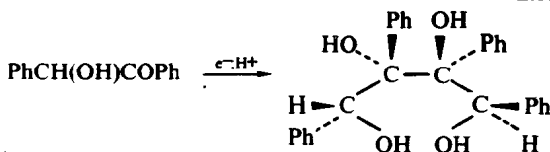
<sup>76</sup> A. P. Tomilov, B. L. Klyuer, and V. D. Nechepurnoi, *Zh. Org. Khim.*, 1975, 11, 1984.

<sup>77</sup> M. Ferles, M. Lebl, P. Štern, and P. Trška, *Coll. Czech. Chem. Commun.*, 1975, 40, 2183.

<sup>78</sup> H. Nohe, F. Beck, W. Dietmar, and E. J. Schier, *Ger. P. 2 345 461 (Chem. Abs., 1975, 83, 9181)*.

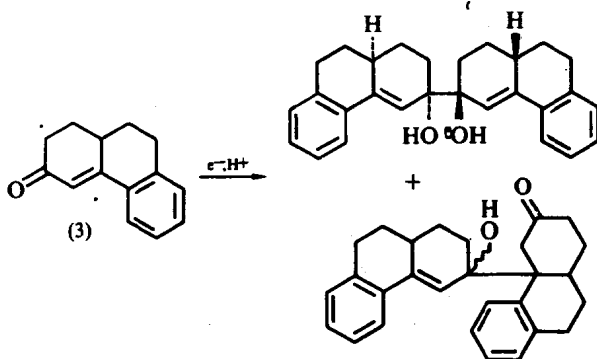
<sup>79</sup> H. Hobe and F. Beck, *Ger. P. 2 343 054 (Chem. Abs., 1976, 84, 10 498)*.

<sup>80</sup> R. E. Juday and W. L. Waters, *Tetrahedron Lett.*, 1975, 4321.



Scheme 8

pinacol by *threo*-coupling, between two molecules of identical enantiomeric configuration (Scheme 9).<sup>81</sup> No other stereoisomers of the pinacol are formed in each



Scheme 9

case, although the enone also gives a mixture of ketols. Pinacol formation has been recorded during the reduction of thiophen-2,5-dicarboxaldehyde,<sup>82</sup> 2-benzoylthiophen,<sup>83</sup> 2-formylselenophen,<sup>84</sup> 2-acetylselenophen,<sup>85</sup> and acetylferrocene.<sup>86</sup>

Studies on the rate of the hydrodimerization of benzaldehyde in sulfolan, using a rotating ring-disc electrode, have been interpreted as showing that there is dimerization of the radical-anion.<sup>87</sup> The radical-anion of 4-nitrobenzaldehyde reacts too slowly for a rate constant to be determined using this technique. 4-Cyanobenzaldehyde undergoes dimerization by the same mechanism at high current densities but by an *ECE* mechanism at low current densities, where the chemical step is reaction between the radical-anion and a neutral molecule.

Reduction of amino-desoxybenzoins is dependent on the pH of the solution.<sup>88</sup> If the pH is sufficiently acid that the amino-function is protonated, then cleavage of the carbon-nitrogen bond occurs, as shown in Scheme 10. In more alkaline solutions this reaction is suppressed, and reduction of the carbonyl group to secondary alcohol occurs, giving a mixture of stereoisomers. Griseofulvin is reduced to dihydrogriseofulvin in aqueous buffer solutions.<sup>89</sup>

Examples have been given of the reduction of carboxylic acid to primary alcohol

<sup>81</sup> E. Touboul and G. Dana, *Tetrahedron*, 1975, 31, 1925.

<sup>82</sup> J. P. Salaun, M. Salaun-Bouix, and C. Caullet, *C.R. Hebd. Seances Acad. Sci., Ser. C.*, 1975, 280, 165.

<sup>83</sup> P. Foulatier, J. P. Salaun, and C. Caullet, *C.R. Hebd. Seances Acad. Sci., Ser. C.*, 1974, 279, 779.

<sup>84</sup> D. Guerout and C. Caullet, *C.R. Hebd. Seances Acad., Sci., Ser. C.*, 1975, 281, 643.

<sup>85</sup> D. Guerout and C. Caullet, *C.R. Hebd. Seances Acad. Sci., Ser. C.*, 1975, 281, 667.

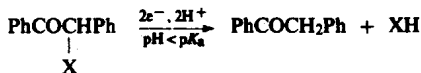
<sup>86</sup> M. Lacan and Z. Ibrisagic, *Croat. Chem. Acta*, 1974, 46, 107.

<sup>87</sup> N. R. Armstrong, N. E. Vanderborgh, and R. K. Quinn, *J. Electrochem. Soc.*, 1975, 122, 615.

<sup>88</sup> J. Armand and L. Boulares, *Bull. Soc. Chim. Fr.*, 1975, 711.

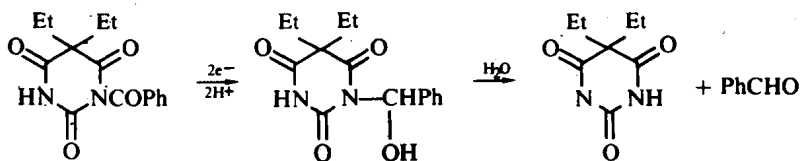
<sup>89</sup> H. J. Baer and E. Beer, *Wiss. Z. Tech. Univ. Dresden*, 1975, 24, 5 (*Chem. Abs.*, 1976, 84, 10 440).





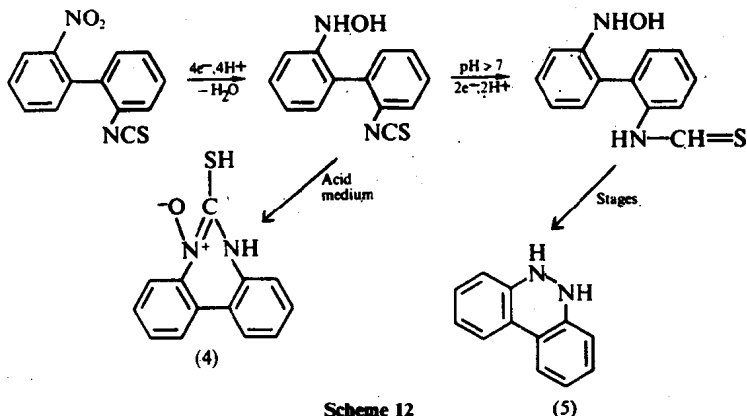
● Scheme 10

in acidic aqueous buffers,<sup>90</sup> reduction of pyridine-2-carboxylic acid and -2,6-dicarboxylic acid, and the reduction of an amide function (see Scheme 11).<sup>91</sup> The reduction of oxalic acid in aqueous solution to glyoxalic acid is the subject of a patent.<sup>92</sup>



Scheme 11

**Nitro- and Nitroso-compounds.**—Reduction of the two nitro-groups in 2,4-dinitrophenol<sup>93</sup> and 2,4-dinitrotoluene<sup>94</sup> to amine has been examined. 3-Nitro-4-hydroxycoumarin is also smoothly reduced to the corresponding amino-compound.<sup>95</sup> Reduction of  $\alpha$ -nitrocinnamic acid methyl ester in acid solution gives ( $\pm$ )-phenylalanine.<sup>96</sup> Reduction of 2-nitro-2'-isothiocyanatobiphenyl causes electrochemically initiated intramolecular cyclization (Scheme 12), and the product depends on the



Scheme 12

<sup>90</sup> O. R. Brown, J. A. Harrison, and K. S. Sastry, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **58**, 387.

<sup>91</sup> W. Pasek, J. Volke, and O. Manousek, *Coll. Czech. Chem. Commun.*, 1975, **40**, 819.

<sup>92</sup> F. Goodridge and K. Lister, Br. P. 1 411 371 (*Chem. Abs.*, 1976, **84**, 66 955).

<sup>93</sup> V. D. Bezuglyi, L. A. Kotok, E. K. Ostis, V. A. Ekel, and R. F. Ramakova, *Khim. Prom-st. (Moscow)*, 1975, 17 (*Chem. Abs.*, 1975, **82**, 161 742).

<sup>94</sup> F. Goodridge and K. C. Nath, *Electrochim. Acta*, 1975, **20**, 685.

<sup>95</sup> M. Trkovnik, M. Lacan, Z. Stunic, and D. Nahmijuz, *Org. Prep. Proced. Int.*, 1975, **7**, 47.

<sup>96</sup> I. A. Avrutskaya, K. K. Babievskii, V. M. Belikov, E. V. Zaporozheto, V. T. Novikov, and M. Ya. Fioshin, *Elektrokhimiya*, 1975, **11**, 661.